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Naval Postgraduate School

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EPITAXIAL VAPOR GROWTH OF
MONOCRYSTALLINE AG FOILS AND THE
DEPENDENCE OF CONDENSATION STICKING
COEFFICIENT ON CRYSTALLOGRAPHIC
ORIENTATION
KENNETH E. CUMBLIDGE

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* * * * *

Kenneth E. Cumblidge

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AND THE DEPENDENCE OF CONDENSATION STICKING COEFFICIENT
ON CRYSTALLOGRAPHIC ORIENTATION

by

Kenneth E. Cumblidge

Lieutenant, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
PHYSICS

United States Naval Postgraduate School
Monterey, California

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This work is accepted as fulfilling
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MASTER OF SCIENCE

IN

PHYSICS

from the

United States Naval Postgraduate School

ABSTRACT

Pairs of thin oriented silver films of different lattice orientation were grown simultaneously by epitaxial condensation. Substrate temperatures of 460°C to 480°C with a deposition rate of 300 to 350 Å per second were found to be the most successful epitaxy parameters. Comparison of the mass of differently oriented pairs grown at symmetrical stations revealed that the condensation sticking coefficient for the (100) plane is consistently about 3.8% less than for the (111) plane, indicating that the condensation sticking coefficient of Ag on Ag is a function of crystallographic orientation.

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1. Introduction.

Epitaxy is the oriented growth of one crystal upon another. While this phenomenon accounts for essentially all crystalline growth, in modern literature the term epitaxy refers to the growth of one crystal upon another of a different species. Ordered deposition of this type on a foreign substrate may be accomplished either from solution or by condensation from the vapor phase.

The physical properties of thin, single crystal, metal films produced by vapor epitaxy are dependent upon the conditions of formation, such as the physical and chemical conditions of the substrate, substrate temperature during deposition, and the rate of deposition (1, 2, 4, 5, 6). A thorough knowledge of the dependence of the physical, chemical, and electrical properties of the films on the conditions of formation is essential to reproducible experimental utilization of the films.

Selection of a proper substrate is to some extent dictated by the subsequent use of the films. Completely oriented metal films have been grown on metals, alkali halides and mica. If separation of film and substrate after epitaxy is required, one must select a substrate that will facilitate this separation. One method is to use a soluble substrate whose solvent is not reactive with the film (1, 2, 6). On the other hand, the formation of an oxide layer between film and substrate will enhance a tight bond, if desired (6). While a small misfit between lattice parameters of substrate and adsorbate seems to enhance epitaxial growth, it is not an essential condition (1).

Preparation of the substrate surface is of prime importance. The ideal surface would be an atomically smooth, bare lattice plane. Cleavage along a lattice plane obtains the most nearly perfect surface. For many

orientations this is not practical. Most surfaces which are prepared by grinding, polishing, or etching are quite rough on an atomic scale. The extent and type of surface preparation after etching is primarily governed by the film properties sought (1, 4, 5, 6). Ion bombardment inside the vacuum chamber is an excellent final cleaning method which removes surface layer contaminants left by the preparatory process (3, 6).

During epitaxy, the rate of deposition in conjunction with substrate temperature influences various film properties. For example, a high rate of deposition will result in a continuous film at a lower thickness, but accelerated nucleation will produce a smaller average grain size (6). A faster deposition rate also requires a higher substrate temperature, so that the adsorbate will have sufficient thermal energy to migrate to a proper lattice site (4, 6).

Oriented films produced by epitaxy are usually highly imperfect. They often contain twins, stacking faults, low angled boundaries, and many dislocations (8). In addition, the films are frequently contaminated with foreign materials. Vaporized material from the crucible in which the charge is melted is an active source of contamination. A large part of this contamination can be prevented if the substrate is shielded from the crucible during epitaxy. Another source of contamination is the residual gas in the evaporation chamber. Yonts and Harrison have investigated the deposition of surface contaminants by the residual gas (3).

Moore, Milne and Harrison (M M H) (9) demonstrated that favorable epitaxy temperatures overlap so that simultaneous epitaxial deposition of Ag on two LiF substrates of different orientation is possible. In this manner they produced oriented pairs of nearly the same thickness (to within a few per cent). In 1962 Takabayashi (5) reported that the

sticking coefficient of Ge on Ge was a strong function of orientation.

M M H established that the condensation sticking coefficient of Ag on Ag was at most a very weak function of crystallographic orientation.

This paper describes in detail the technique used to produce pairs of oriented Ag films for investigation of range-energy relations of protons in silver as a function of crystallographic orientation. The requirement that the films be separable from the substrates resulted in a compromise between film quality and ease of separation. While this paper makes no attempt at a theoretical analysis of the mechanism of variable sticking coefficient, it does explore the relative sticking coefficients for the 100 and 111 orientations.

2. Apparatus.

The apparatus consists of a control console containing the necessary vacuum and electronic equipment; a bell jar evaporation chamber containing the crucible, the furnace with associated substrate clamping mechanism, and the crucible shielding device; and a thermocouple circuit temperature monitor (Figs. 1 through 4). The furnace and all associated parts are fabricated of stainless steel to minimize contamination by vaporization of foreign material. The furnace element is number 14 nichrome wire insulated by fish spine ceramic beads. A stainless steel trap suspended through the top of the bell jar (sealed by a viton gasket) served as the furnace support.

The substrate clamping mechanism, as illustrated in Fig. 3, is designed to exert equal clamping pressures on substrates of slightly different thicknesses, thus equalizing the thermal conduction conditions from the furnace to each substrate. The masks were precision reamed and beveled to prevent shadowing the substrate.

As shown in Figs. 3 and 4, the stainless steel shield minimizes contamination from the crucible, aids in geometrical alignment, improves the presentation of a point source, and protects the substrate from most of the heat radiated from the crucible.

The thermocouple which monitors the substrate temperature is held in place by a titanium clamp (Figs. 3 and 4).

The Ag charge is vaporized in a tantalum crucible, with elbow joints in the crucible arms which permit thermal expansion but maintain the alignment of geometry.

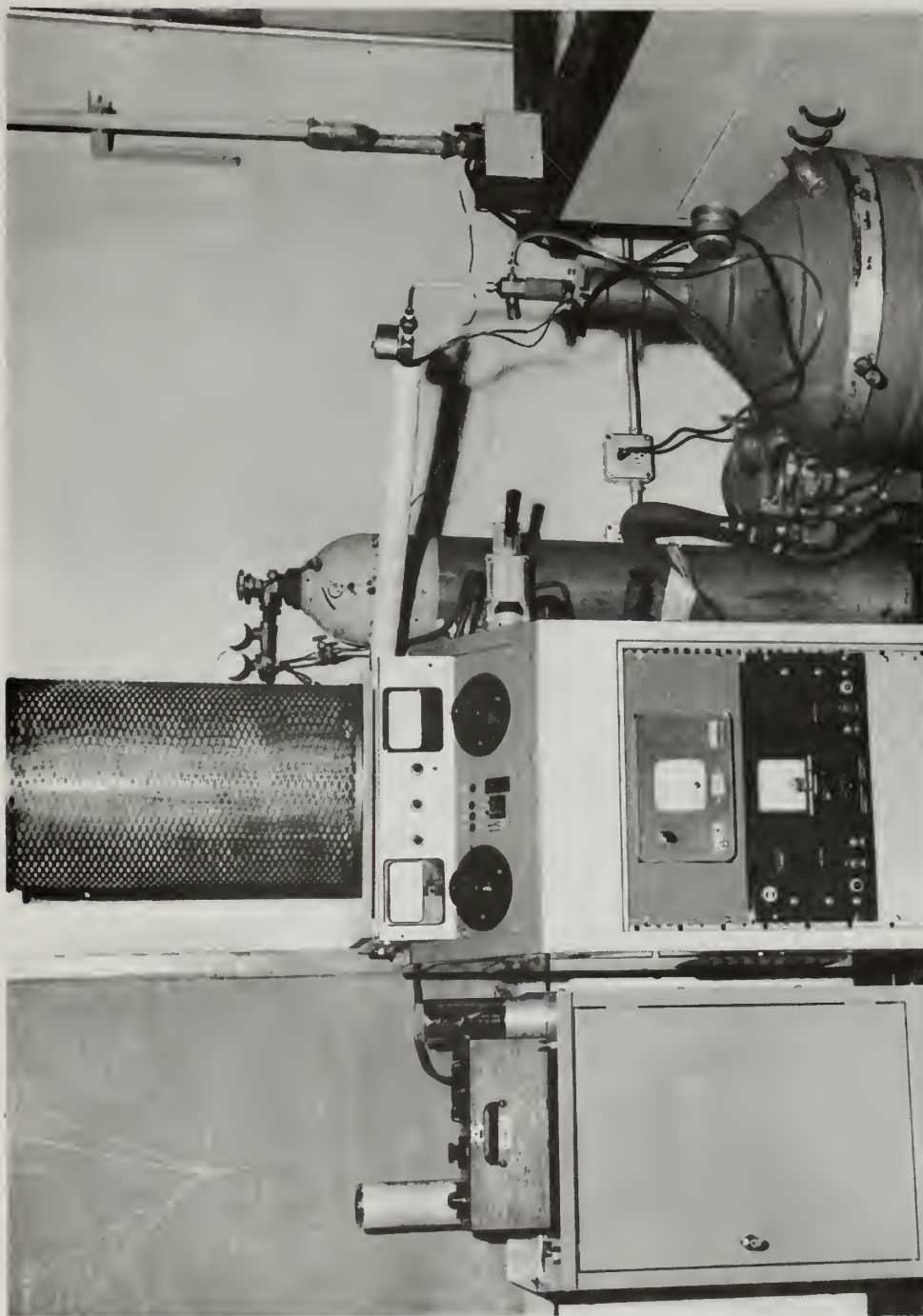


Figure 1. Evaporation console and associated equipment.

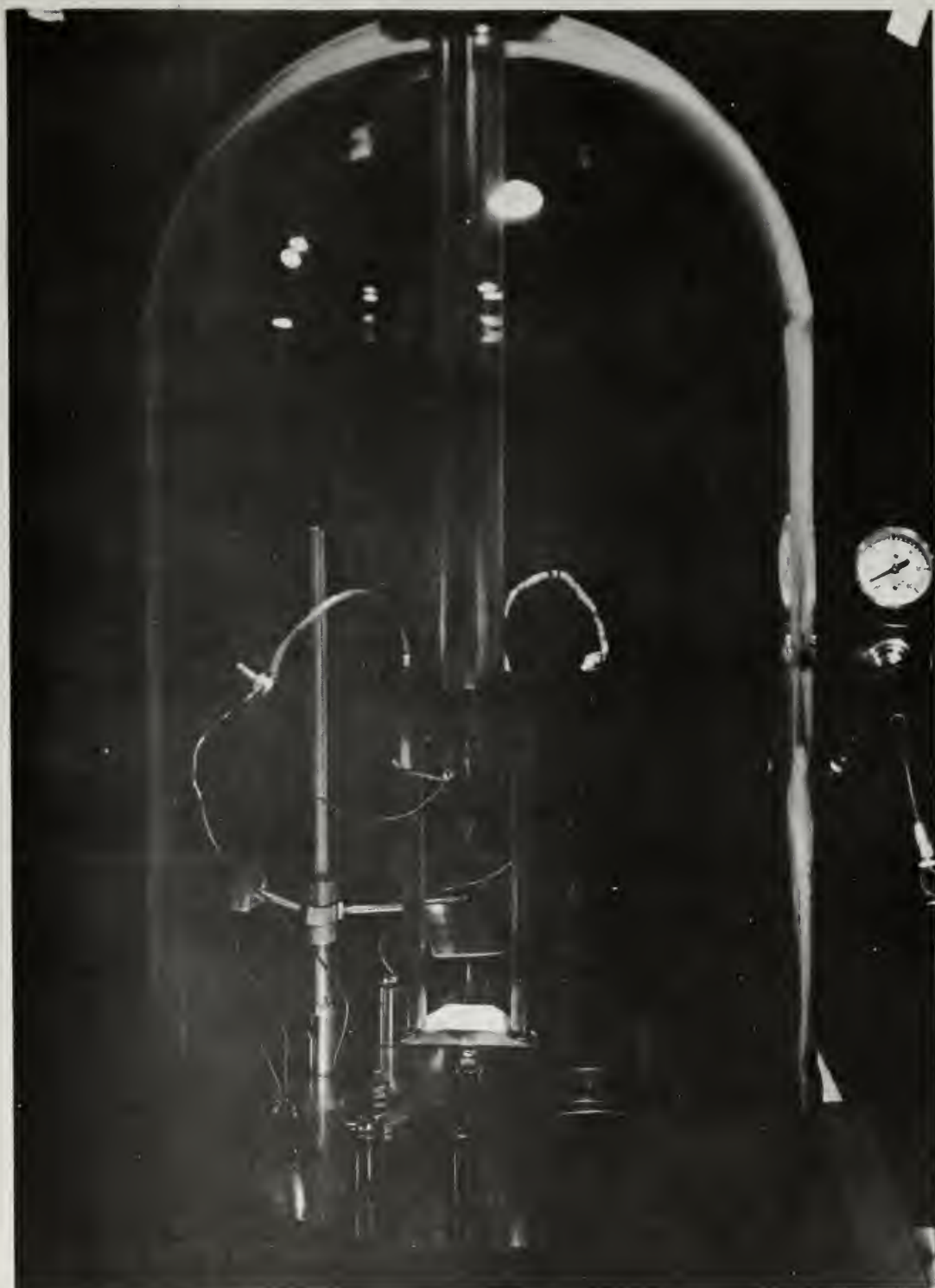


Figure 2. Evaporation chamber with apparatus assembled.

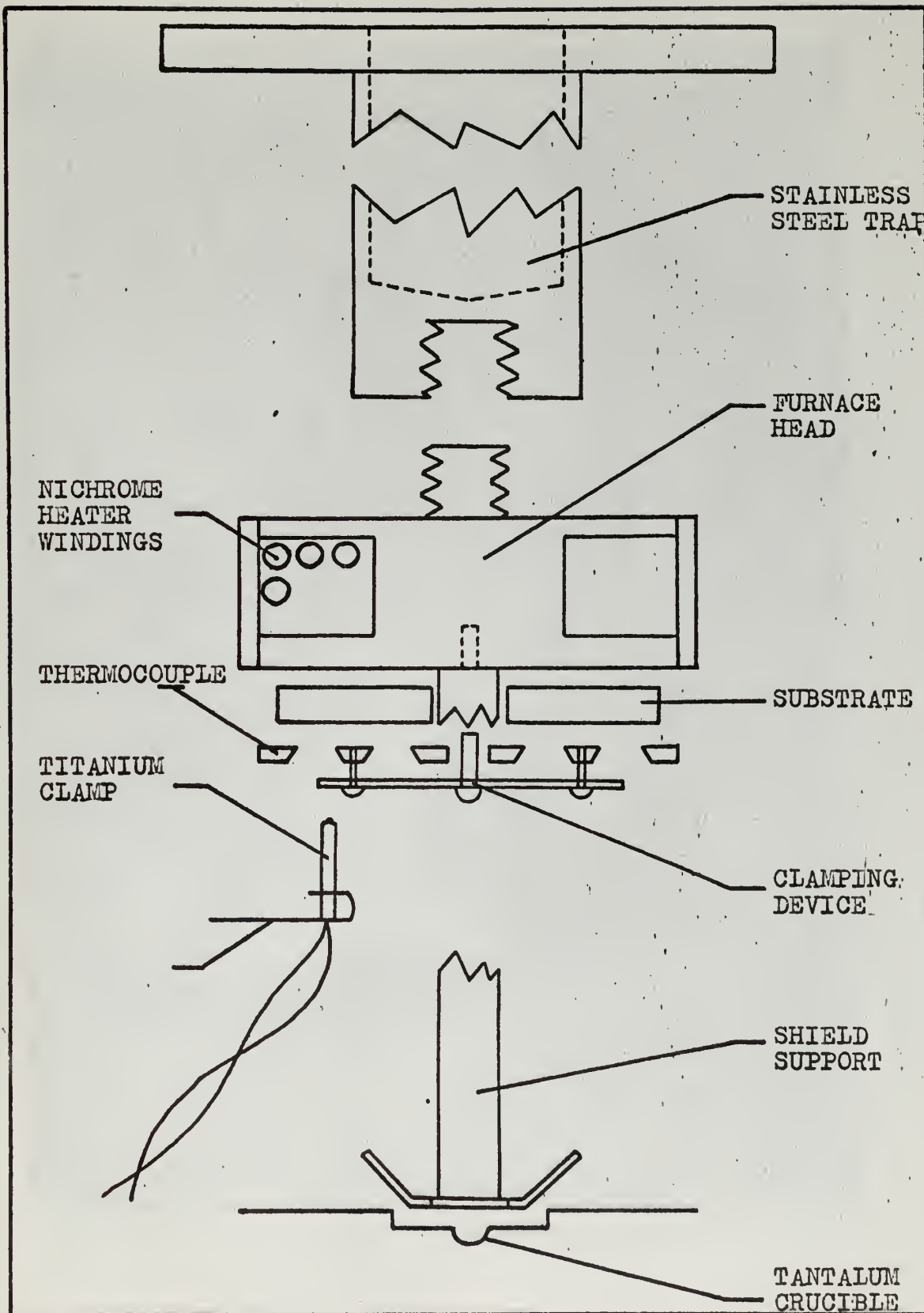


Figure 3. Furnace Assembly

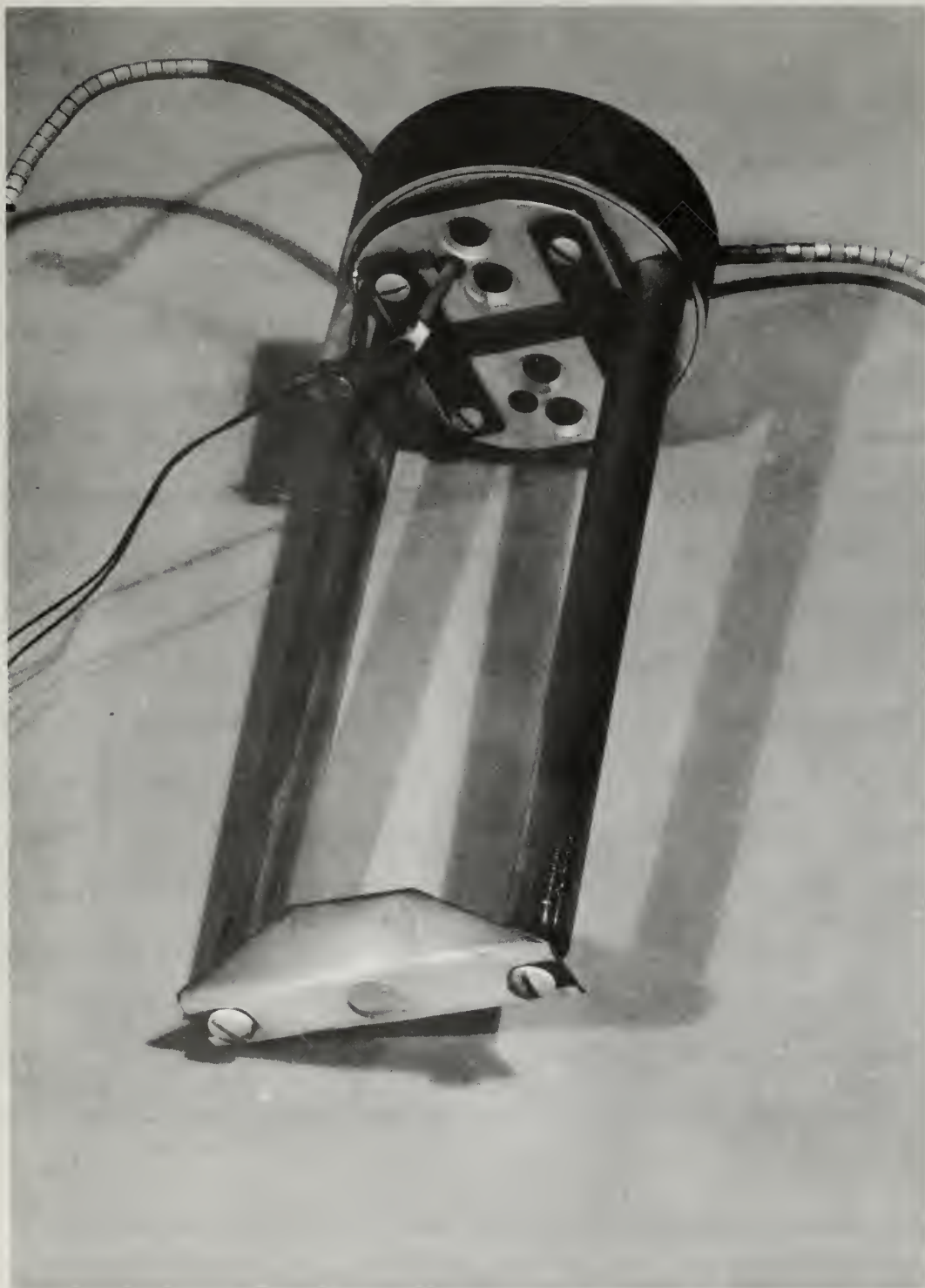


Figure 4. Furnace, with substrates mounted and thermocouple in place

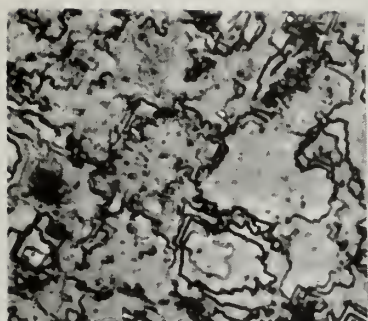
3. Experimental Procedures.

As mentioned above, it was necessary to remove the films from the substrates after epitaxy. The M M H experimental procedures were used, with a few modifications.

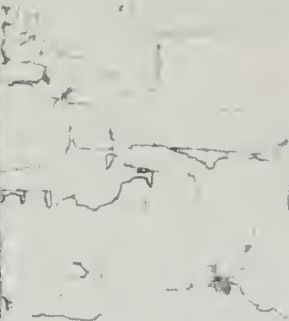
The importance of proper substrate preparation cannot be over-emphasized. Obviously, if a polycrystalline surface is presented, a polycrystalline film will be grown. In the present experiments all substrates were disk shaped (1 inch diameter and 6 mm thickness), commercially available LiF crystal blanks. The surfaces were ground as flat as possible on a 3 micron diamond wheel and smoothed on a 1 micron wheel. They were then etched with hydrofluoric acid and chemically polished with ammonium hydroxide solution (7). The degree of etching and chemical cleaning is a critical factor in the extent of film orientation. Etching for one minute in HF1 proved to be satisfactory for all three orientations (111, 110 and 100), but the degree of chemical cleaning required to flush all polycrystalline debris from the surface seemed to depend on several unknown factors, such as temperature of NH_4OH solution, age of solution, etc. The time required for cleaning in vigorously stirred NH_4OH solution ranged from 5 to 15 minutes. Figs. 5a through 5c show surface conditions after various degrees of cleaning.

Further cleaning of surface by ion bombardment or other means was undesirable, as too tight a bond might result. The films were separated from the substrates after soaking in lightly stirred distilled water for a few hours.

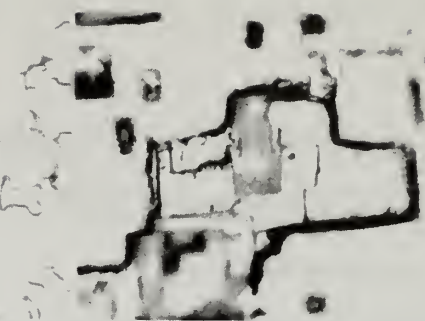
The prepared substrates were washed with anhydrous reagent ether, dried by a stream of hot, dry air which also removed any dust, and clamped to the furnace as shown in Figs. 3 and 4. The furnace was



under etched



properly etched



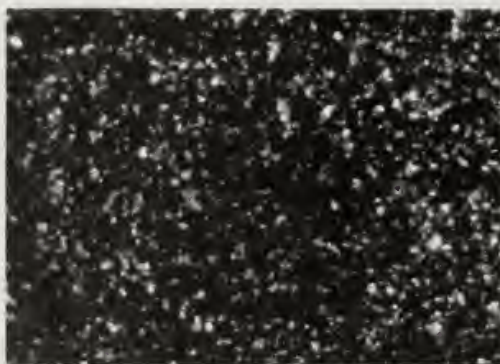
over etched

a. (100)



properly etched

b. (110)



properly etched

c. (111)

Figure 5. Micrographs of substrate surfaces after etching and cleaning. (500X)

aligned with the crucible centered about 6 mm below a .5 inch hole in the shield suspended from the furnace. The distance from crucible to furnace was 19.5 cm. The Ag used is commercially available and specified to be 99.99% pure.

While the chamber was pumped to vacuum, the temperature of the furnace was slowly increased to the epitaxial range (approximately 15°C per minute). An excessive heating rate causes a more rapid expansion of the substrates than of the clamping mechanism, and the resultant clamping pressures crack the LiF crystal blanks.

After the substrate temperature had stabilized in the desired range, and the chamber pressure had reached 10^{-6} torr or slightly lower, the crucible was heated to about 900°C to allow the crucible and Ag to outgas. When the vacuum gauge indicated that essentially all outgassing was complete, the temperature of the crucible was raised to the melting point of Ag, but a shielding plate between crucible and furnace was kept in place for 15 seconds to protect the substrates while any volatile impurities evaporated. The current to the crucible was then increased to produce the desired evaporation rate, and the shielding plate was pivoted to one side.

All heating was stopped immediately upon completion of evaporation. After the substrates had cooled to 400°C, liquid nitrogen was poured into the stainless steel furnace support to assist cooling. About 5 torr of helium was admitted at 200°C to facilitate cooling. After reaching room temperature, the substrates were removed and soaked in lightly stirred distilled water for film removal (7).

The films were weighed with a precision electrobalance to within two micrograms, mounted in stainless steel holders, and examined for extent and quality of orientation by Laue X-ray transmission patterns.

4. Results.

Epitaxy temperatures reported by M M H were used, but the deposition rate was considerably higher. A substrate surface temperature of 460°C to 480°C with a deposition rate of $300\text{-}350 \text{ \AA}$ per second was found to yield well-oriented films for all three orientations (100, 110 and 111). Examples of the Laue X-ray patterns of the films are shown in Figs. 8 and 9.

It is difficult to judge whether a thin film is a continuous or a large-grained crystal. Stacking faults obviously exist where growth areas have joined. The area of the X-ray beam used to analyze the films was about 3mm^2 , which is many orders of magnitude greater than a finely collimated ion beam; hence the films that presented acceptable Laue patterns would present a single crystal structure for subsequent sputtering experiments. Lack of proper equipment precluded further analysis of the quality of the films.

With proper alignment and symmetry, the two substrates would "see" the same total integrated flux from the vaporized Ag charge. If the sticking coefficient for Ag on Ag is identical for different orientations, then the films grown at stations $A_1 - B_1$, and stations $A_2 - B_2$ (see Fig. 6), should have identical masses to within experimental error. Results of five evaporations are shown in Table I and in Fig. 7 as a plot of mass difference as a function of average mass for each 111-110 pair. The data from each evaporation are averaged to distribute the geometrical error.

The first four evaporations were conducted with the substrates at a distance of 19 cm, while the fifth evaporation was at 15 cm. The decrease in distance was necessary to obtain sufficient total integrated Ag flux.



An alternative would have been to increase the size of the crucible to accommodate a larger Ag charge, but this would have introduced more geometrical uncertainty than decreasing the crucible to substrate distance.

Considering only the first four runs, the data indicate that the growth rate, and hence the sticking coefficient, of the (100) orientation is consistently 3.9% less than that of the (111) orientation. Including the data of the fifth run (conducted under different geometrical conditions) decreases the difference to 3.7%.

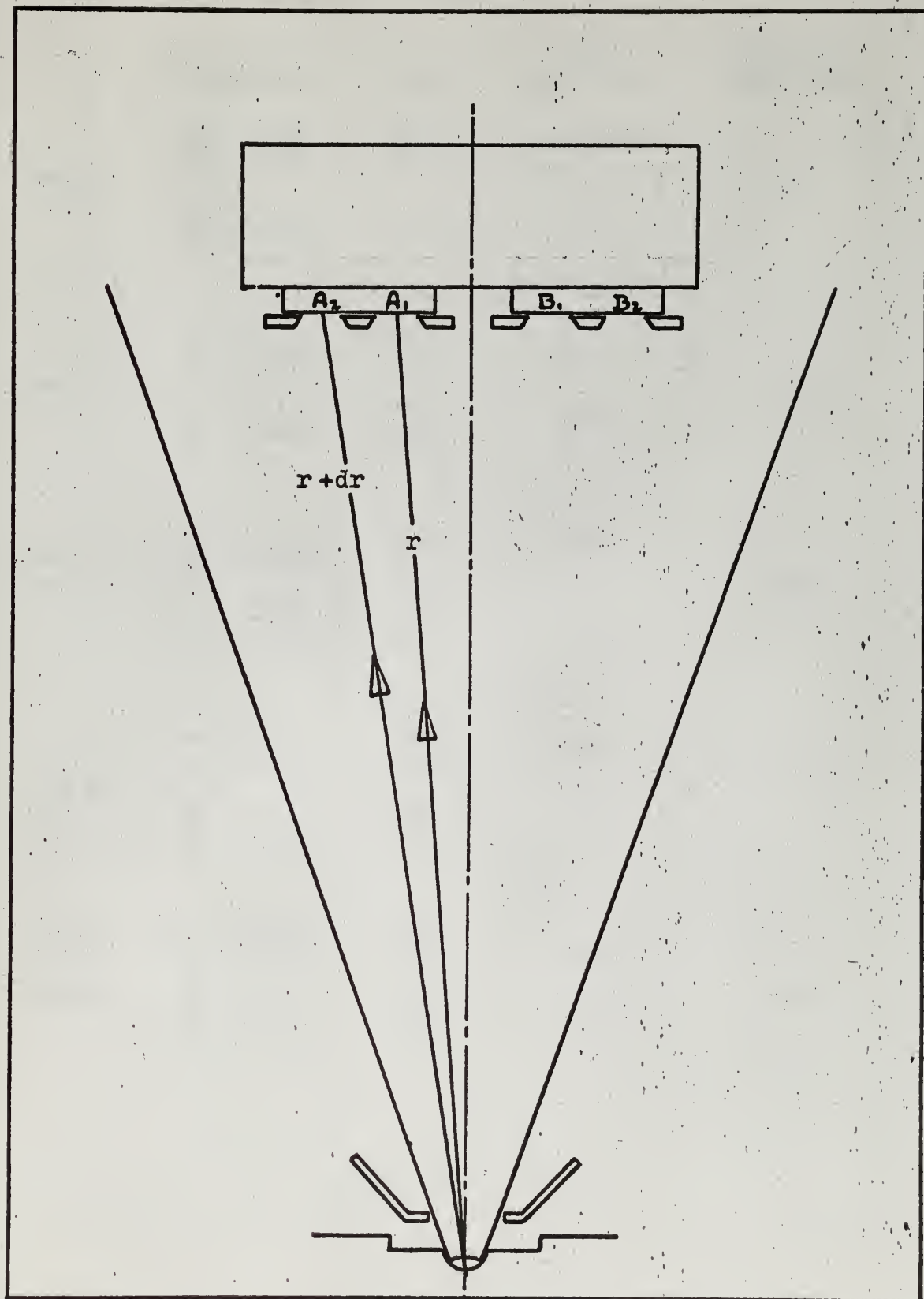


Figure 6. Geometry of Ag flux emission

TABLE I

	Orientation	Mass	Mass Difference	Average Mass Difference
Run #1	A ₁ - (111)	317 mg	3.2%	3.2%
	B ₁ - (100)	307		
	A ₂ - (111)	-	-	
	B ₂ - (100)	305		
Run #2	B ₁ - (111)	587	3.1%	3.45%
	A ₁ - (100)	569		
	B ₂ - (111)	565	3.8%	
	A ₂ - (100)	544		
Run #3	A ₁ - (111)	848	4.3%	4.2%
	B ₁ - (100)	810		
	A ₂ - (111)	819	4.1%	
	B ₂ - (100)	786		
Run #4	B ₁ - (111)	1029	3.9%	4.15%
	A ₁ - (100)	991		
	B ₂ - (111)	973	4.2%	
	A ₂ - (100)	933		
Run #5	A ₁ - (111)	1591	2.8%	3.2%
	B ₁ - (100)	1547		
	A ₂ - (111)	1419	3.6%	
	B ₂ - (100)	1369		

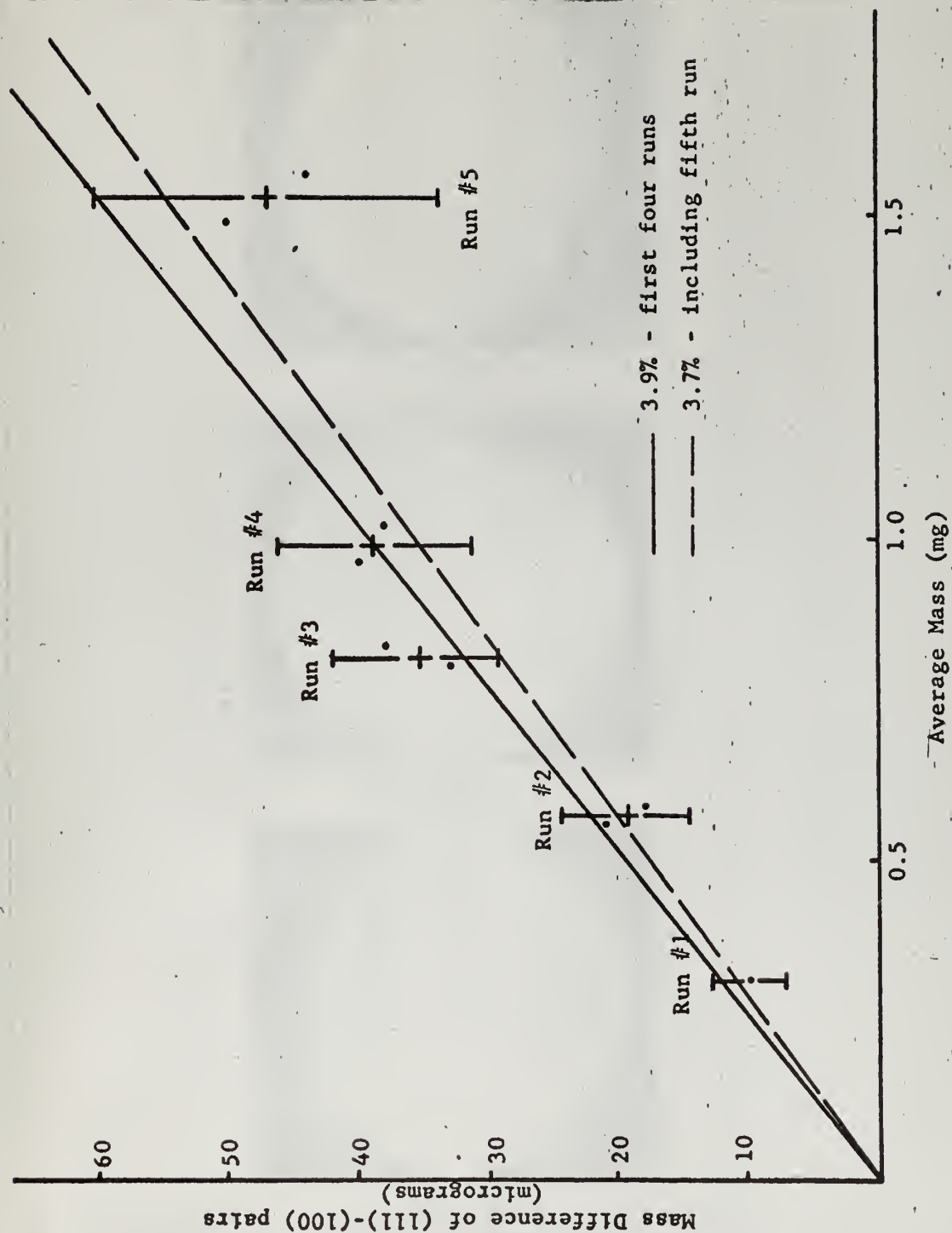


Figure 7. Mass difference as a function of average mass for (111) - (100) pairs.



a. (111)



b. (110)



c. (100)

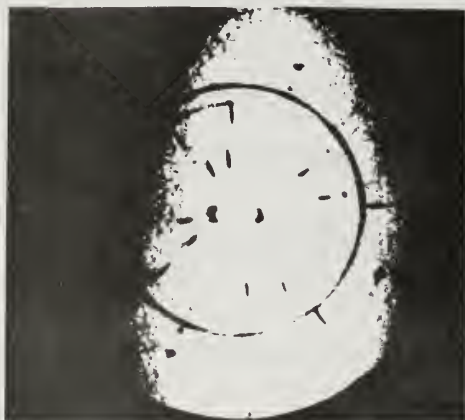
Figure 8. Laue transmission patterns of (111), (110) and (100) orientations.



a. (111) with Debye-Scherrer rings



b. (110) considerably stressed



c. (100) with Debye-Scherrer rings and slightly stressed

Figure 9. Laue transmission patterns with Debye-Scherrer rings

5. Analysis of Results.

If the Ag vapor were distributed uniformly and spherically from a point source, the total flux arriving per unit area at a distance r would be:

$$\Phi = \frac{w}{4\pi r}$$

where w is the mass of the Ag charge in grams. Uniform 2π emission would result in twice the flux density, or

$$\Phi = \frac{w}{2\pi r^2}$$

The shape of the crucible modifies this distribution, and the Ag vapor is emitted through a solid angle somewhat less than a hemisphere, with decreased density in the peripheral region.

In the central region the flux density is considerably higher than 2π distribution. If the flux in the vicinity of the substrates is uniform, a distribution factor can be assigned, and

$$\Phi = \frac{1}{A} \frac{w}{4\pi r^2}$$

where the distribution factor A would be $1/2$ for 2π emission. For small changes in r , the change in Φ would be:

$$d\Phi = \frac{1}{A} \frac{w}{4\pi r^2} \left(-\frac{2dr}{r} \right)$$

Thus, the fractional change in Φ for small variations in r would be:

$$\left| \frac{d\Phi}{\Phi} \right| = \frac{2dr}{r}$$

Accordingly, a misalignment of the crucible by 2 mm off center at a distance of 19 cm would introduce a difference of about 0.7% in the flux

density at stations A_2 and B_2 (see Fig. 6), and a difference in substrate thickness of 0.2 mm would result in 0.1% difference. Thus, an estimate of maximum geometrical error is 0.8%.

If the Ag vapor were emitted uniformly throughout the solid angle subtended by the substrates, the difference in total integrated flux arriving at stations A_1 and A_2 on the same substrate would be attributable to the difference in radial distance from the crucible. Adjacent films on the same substrate (obviously with the same sticking coefficient) would then differ in mass by approximately 0.8%. Table II shows the experimental difference in mass of the films grown at adjacent stations on the same substrate for the five evaporations of Table I. The average difference of 4.6% suggests that the shape of the crucible has a pronounced focusing effect, and the flux density is greater toward the center. Comparison of the mass difference between stations $A_1 - A_2$ and stations $B_1 - B_2$ for each evaporation shows that the focusing is symmetrical.

To determine if this focusing effect would introduce further error, several test evaporations were conducted with (100) substrates in both positions. Comparison of the masses of symmetrical pairs verified that the error attributable to misalignments in geometry was consistently less than 1%.

The experimental data of Table I (displayed in Fig. 7) indicate a consistent mass difference of about 3.8% between pairs for the (111) - (100) orientations. These data clearly indicate that the condensation sticking coefficient for Ag on Ag is a function of crystallographic orientation.

TABLE II

	Stations	Percent Mass Difference
Run #1	$A_1 - A_2$ (111)	-
	$B_1 - B_2$ (100)	1.0%
Run #2	$A_1 - A_2$ (100)	4.4%
	$B_1 - B_2$ (111)	3.8%
Run #3	$A_1 - A_2$ (111)	3.5%
	$B_1 - B_2$ (100)	3.0%
Run #4	$A_1 - A_2$ (100)	6.0%
	$B_1 - B_2$ (111)	5.6%
Run #5	$A_1 - A_2$ (111)	5.0%
	$B_1 - B_2$ (100)	5.3%

6. Recommendations.

I feel that with some refinement in technique, and a few modifications to existing apparatus, further investigation of the production of single crystal films for sputtering experiments and continued efforts to establish sticking coefficient relations would be rewarding and is well warranted.

Foremost I would recommend that the evaporation chamber be converted to a cylinder with a circular stainless steel top. This would render the apparatus operatable by one attendant, decrease the size of the vacuum chamber, make possible the installation of a cold trap, and facilitate cleaning. Secondly, I would suggest that the chamber be modified to accommodate a second crucible, to enable investigation of the technique of evaporating a thin metallic film as a substrate.

If an electron microscope were available for analysis of the films grown, considerably more data would be available.

7. Acknowledgements.

The author deeply appreciates the counsel and encouragement of his advisors, Associate Professor E. A. Milne and Associate Professor D. E. Harrison, Jr. The instruction of Professor J. R. Clark in X-ray analysis and technique was most helpful. Thanks are also due to technicians R. A. Garcia, who did an excellent job in building the evaporation console, D. Clark, for his valuable suggestions on substrate etching techniques, M. J. O'Dea, whose patience in fabricating furnace parts was unending, and K. C. Smith and M. J. Andrews, who provided invaluable assistance on related problems.

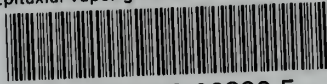
Appreciation is also extended to my wife for her tolerance.

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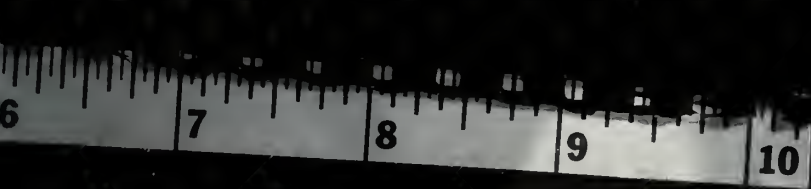
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